REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-07-0130

1. REPORT DATE (DD-MM-YYYY) 03-31-2007	2. REPORT TYPE Final	3. DATES COVERED (From - To) Jan-1-05 to Dec-31-06

4. TITLE AND SUBTITLE
Final Technical Report:

First principles and multi-scale modeling of the roles of impurities and dopants on thermal barrier coating failure

5a. CONTRACT NUMBER

5b. GRANT NUMBER
FA9550-05-1-0119

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Emily A. Carter

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Princeton University   Department of Mechanical and Aerospace Engineering, Suite D404a
Olden St, Princeton, NJ 08544

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Office of Research   801 N.Randolph St. Rm732
Arlington, VA 22203-1977

Dr Michael Berman/NL

10. SPONSOR/MONITOR'S ACRONYM(S)
AFOSR/NL

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT Optimization of thermal barrier coating materials is the main objective of this research, in order to increase the service lifetimes of aircraft engines. To this end, it is critical to first understand mechanisms of failure, and then use those insights to design materials countermeasures. This grant supported the following research efforts in those directions:
- Developments of ultrasoft spin-dependent pseudopotential theory and a solid state phase transition path search algorithm
- Applications of first principles density functional theory to:
  - monoclinic-to-tetragonal phase transformation pathway in zirconia
  - atomic scale fatigue in silicon and alumina
  - metal-ceramic interfaces ($MoSi_2/SiO_2$ and $NiAl/Al_2O_3$)
  - adsorption of dopants (Hf, Pt) and impurities (S) on NiAl and segregation of same to $NiAl/Al_2O_3$ interface
  - formation and segregation of impurities, dopants, defects, and majority species in NiAl and alumina
  - dopants added to alumina/late transition metal interfaces, with implications for high temperature catalysis

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Michael Berman
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			19b. TELEPHONE NUMBER (include area code) 703-696-7781

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

FINAL REPORT

TO THE

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

Emily A. Carter

Principal Investigator

Department of Mechanical and Aerospace Engineering
and Program in Applied and Computational Mathematics
Princeton University, Princeton, NJ 08544-5263

Grant No. FA9550-05-1-0119

March 31, 2007

20070426201

1

Jet turbine engine metal components are protected by a multilayer, multi-component thermal barrier coating (TBC), formed by sequential deposition of a NiAl-based bond coat alloy followed by plasma spray or electron beam deposition of yttria-stabilized zirconia (YSZ). A layer of alumina grows in between these two materials during YSZ deposition and grows further during use. Present TBCs spall off after ~16,000 hrs of thermal cycling, forcing the engine to be removed from service. If more robust TBCs can be designed, the engine could operate at higher temperature, providing either increased fuel efficiency or greater thrust. Preventing or further delaying coating failure is the main goal of this research, in order to increase the service lifetimes of aircraft engines. Our strategy is to first identify inherent causes of TBC failure and then use that insight to suggest improved TBC materials that could extend coating lifetimes.

Thermal cycling exposes the TBC to repeated expansion-contraction cycles, as well thermally-initiated diffusion and possible phase transformations, which ultimately results in spallation of the coating. TBC failure may be triggered by several events originating at the atomic scale: (i) thickening of the alumina layer via O and Al atom diffusion from the air and bond coat alloy, respectively, subsequently producing growth and thermal stresses that ultimately cause spallation at the alumina-bond coat alloy interface; (ii) impurity-induced spallation, where adhesion of the alumina scale to the bond coat is compromised by elements that segregate to the interface by high temperature diffusion; (iii) fatigue cracking of alumina due to stresses induced by the mismatch in thermal expansion coefficients between the alumina scale and the bond coat alloy; and (iv) phase transformations due to yttrium ion segregation, producing pure zirconia domains that transform between monoclinic and tetragonal phases upon thermal cycling.

We summarize on our research into each of these failure modes, where first principles quantum mechanics (density functional theory, DFT) is employed to examine them. However, we first report the publication of two new theoretical methods now used to explore TBC materials: a solid state transition state search algorithm for solid-solid phase transformations and an ultrasoft spin-dependent pseudopotential theory. These methods were used to identify the monoclinic to tetragonal phase transformation pathway in zirconia (yielding insight into the observed temperature hysteresis) and to efficiently and accurately predict transition metal properties, respectively. We then outline findings on microscopic mechanisms of fatigue cracking in alumina and silicon. We next discuss a possible alternative protective coating design, involving $MoSi_2$, which might be deposited on top of the bond coat alloy or the superalloy. We then report characterization of impurities (S) and dopants (Hf and Pt) known to be present at the surface of the NiAl bond coat, and how these elements affect adhesion at the $NiAl/Al_2O_3$ interface. Lastly, we discuss ongoing work uncovering impurity and dopant segregation and diffusion mechanisms in alumina and NiAl and their implications for

TBCs. We then present a list of personnel involved and end with a publication list where more details may be found. Citation numbers given refer to the publication list.

Transition State Search Algorithm for Phase Transformations in Crystals

We developed a technique to find minimum energy paths (MEPs) for martensitic solid-solid phase transformations, allowing us to quantify transformation activation energies and elucidate microscopic mechanisms of such transitions [1]. The monoclinic-to-tetragonal transformation in zirconia falls into this martensitic class, and our desire to study it was the primary motivation behind the development of this technique. We generalized a method developed earlier for identifying chemical reaction MEPs: the Climbing Image Nudged Elastic Band (CI-NEB) algorithm. Our extension of CI-NEB accounts for the deformation of the crystal lattice (volume and shape fluctuations) along the transition path, by recasting atomic force-displacement space into crystalline stress-strain space. Then we use our solid state NEB (SS-NEB) method to search the stress-strain energy landscape for saddle points where the stress is zero, as well as optimizing the MEP in this space. We introduced an analog to the Born-Oppenheimer approximation that allows a decoupling of nuclear motion and lattice deformation. The decoupling assumes that lattice deformation is much slower than atomic motion and hence the atomic motion is equilibrated for each lattice deformation. This allows us to define a unique MEP, where only the lattice degrees of freedom define the transformation coordinates.

Ultrasoft Spin-Dependent Pseudopotential Theory

We demonstrated a few years ago that use of spin-dependent pseudopotentials (SDPs) markedly enhances the accuracy of pseudopotential DFT predictions of properties of transition metals. Since the major component of jet engines is nickel, and nickel is magnetic, accurate treatment of its magnetic behavior is essential. Our original SDP theory was based on expensive norm-conserving pseudopotentials. The current work extends the SDP theory to exploit the computationally efficient ultrasoft formalism and shows that it is simple to add such a feature to current DFT codes [2]. We benchmarked our ultrasoft SDP theory and then applied it to a variety of transition metal systems. Most strikingly, we showed that while conventional ultrasoft pseudopotentials do not describe all phases and magnetic properties of Fe correctly, our ultrasoft SDP theory produces equations of state for all phases and magnetic states of Fe in excellent agreement with all-electron DFT, but at less cost.

Monoclinic-to-tetragonal phase transformation pathway in zirconia

As mentioned above, one contribution to TBC failure could be diffusion of yttrium ions in YSZ, which could produce pure zirconia regions in the TBC top coat. The pure ZrO_2 then would undergo phase transformations upon thermal cycling,

building up stress in the TBC (since monoclinic m-ZrO$_2$ is 4% larger than tetragonal t-ZrO$_2$), eventually leading to failure. The relevant transformation takes m-ZrO$_2$ at ambient pressures and room temperature to t-ZrO$_2$ at temperatures above 1170 °C. Interestingly, t-ZrO$_2$ does not transform back to m-ZrO$_2$ at the same temperature upon cooling. It exhibits a significant hysteresis, only transforming back to monoclinic at several hundred degrees lower temperature. This strongly suggests the presence of a kinetic barrier. Other than its known martensitic behavior, the atomic scale pathway converting 7-coordinate Zr ions in m-ZrO$_2$ to 8-coordinate Zr ions in t-ZrO$_2$ is unknown. We applied our SS-NEB method to this phase transformation using DFT, and were able to characterize the pathway by which the transformation occurs [3]. The transformation is found to be significantly activated (6.5 meV/ZrO$_2$) compared to barriers we've found for martensitic transformations in metals, consistent with the very high temperature required under ambient pressures for this transformation to occur.

Starting from m going to t, or vice-versa, the beginning stages of the transformation are predicted to be almost purely elastic, with the energy increasing quadratically and stress increasing quasi-linearly. Over a very narrow range of strains, the stress changes discontinuously and the ion positions also change rapidly around the saddle point. The coordination number around Zr changes rapidly from 7 to 8 upon going from m to t ZrO$_2$ over this small strain range. Accordingly, the transformation is predicted to occur discontinuously, which may be the origin of the temperature hysteresis. The nature of transformation path, where elastic deformations of either equilibrium phase bring the material close to the transition state, but where a stress buildup is required to overcome the barrier, may cause a lag in the transformation trajectory. This is in contrast to metallic phase transitions, where we find stress changes are usually smooth and gradual. The difference in behavior is due to the localized mixture of ionic and covalent bonding in ZrO$_2$, which makes it difficult to change coordination number (strong bonds must be rearranged, leading to a large barrier).

Atomic Scale Fatigue in Silicon and Alumina

In work related to microelectronics and to TBCs, we used DFT to explore the effect of cyclic tensile loading on silicon [4] and alumina [5], as representative covalent and ionic materials. We explored their behavior in the threshold region of crack formation, i.e., where the crystal must choose between healing a defect through a uniform elastic strain of the material or breaking bonds to create two free surfaces. We found evidence for nanoscale fatigue when the silicon or alumina lattice is subjected to uniaxial tensile loading and unloading; defects are formed such that the crack cannot heal upon unloading. It is likely that such atomic scale fatigue impacts the durability of ceramics and semiconductors in general, since the localized bonding in both material families requires very specific lattice structures in order to maintain cohesive strength.

For silicon, dangling bonds are created that quickly create new Si-Si bonds to lower the surface energy, but then these new bonds are not easily broken upon unloading to form the perfect crystal again. Rather, the healed crack interface contains defects, placing the flawed energy minimum at a finite strain of 3% and an increased energy of 1.13 J/m^2 relative to the defect-free bulk crystal configuration. The irreversible plastic deformation we observed supports a mechanism proposed by experimentialists that invokes mechanically-induced subcritical cracking to explain the delayed onset of failure in silicon microdevices.

For alumina, the atoms also rearrange significantly upon uniaxial loading and subsequent crack formation. Upon unloading, the crack cannot re-heal perfectly, leading to a weakened crystal (i.e., fatigue). However, we find this effect occurs only when the crack planes normal to the applied load are also under tension, which is the typical case around a crack tip. We observed hysteresis in the pathway followed by the ions under cyclic loading. The origin of this hysteresis appears to be due to the fact that the atomic structure along the path depends on specific local crack surface relaxations. Nonequilibrium atomic structures are formed upon crack healing that are weaker than the equilibrium one, leading to fatigue.

Alternative Protective Bond Coating: MoSi$_2$

Our earlier work highlighted the importance of localized covalent or open-shell interactions across heterogeneous interfaces to enhance adhesion. We proposed that replacing alumina with a more covalent oxide may help TBC adhesion. Due to its propensity to limit bulk oxygen transport similar to that of alumina (alumina's main purpose in the TBC), we considered silica as a possible replacement oxide. We found that the more covalent silica coating is much more strongly adhered to both ZrO$_2$ and to a Ni substrate (models of YSZ and the Ni alloys used in TBCs, respectively). In order to consider SiO$_2$ further, a metal silicide must be found that could provide the source of Si to be oxidized to silica. MoSi$_2$ has a high melting point (2030 °C) and high-temperature oxidation resistance. It does have a brittle-to-ductile transition in the range of 1000 °C to 1400 °C, which could be problematic, but perhaps its mechanical properties can be optimized in a thin film or composite. Its oxidation resistance results from a protective silica scale.

We used DFT to examine the interface between SiO$_2$ and MoSi$_2$ [6]. We found that the interfacial bonding is localized, as evidenced by an adhesion energy that changes only slightly with SiO$_2$ thickness. The adhesion energy displays a rather large (0.40 J/m^2) variation with the relative lateral position of the SiO$_2$ and MoSi$_2$ lattices due to changes in Si-O bonding across the interface. The most stable interfacial structure yields an extremely high ideal work of adhesion of ~5 J/m^2, due to formation of strong covalent Si-O bonds across the interface. The strong adhesion of the SiO$_2$ scale to MoSi$_2$ further supports the potential of MoSi$_2$ as a high-temperature structural material and coating.

If this multilayer material is coupled to the YSZ TBC topcoat, where we previously showed that zirconia binds strongly to silica, this three-tier coating could be a viable alternative to the bond coat/alumina/zirconia coating currently used in TBCs.

Adsorption of S impurities and Hf and Pt dopants on the NiAl(110) Surface

The key interface that controls spallation of TBCs is the interface between the thermally grown oxide (TGO) and the bond coat alloy. The TGO is known to be primarily α-alumina, which is how it is modeled in all our work. The bond coat alloy is a nonstoichiometric NiAl alloy containing either ~5 at% Pt in the platinum aluminide bond coats or Cr and Y in the NiCrAlY bond coat family, with other elements added as dopants as well. In past work, we modeled the bond coat alloy as pure Ni with surface dopants. We now study the closest-packed (110) surface of β-NiAl, as a more refined model of the bond coat alloy surface.

Our DFT calculations provide an excellent description of both the bulk and surface properties of NiAl, reproducing the bulk lattice parameter and modulus to within 1% of experiment and the observed rippling of the (110) surface, in which Al atoms move outward and Ni atoms move inward. These results [7] lend confidence in using DFT to study adsorption of relevant segregating elements on this surface.

Hf is a common dopant in NiCrAlY bond coat alloys, Pt is central to NiPtAl bond coats, while S is an impurity derived from the manufacture of the Ni superalloy jet engine components. It is thought that S segregates to the bond coat alloy/TGO interface. Thus all three elements Hf, Pt, and S are of interest to characterize from the standpoint of optimizing TBCs. We used DFT to compare their adsorption on NiAl(110) [7]. We find that while S adsorbs in a three-fold site, the metals prefer to adsorb in the Ni-Ni two-fold bridge site, consistent with scanning tunneling microscopy of transition metals adsorbed on NiAl(110). We find Pt favors interaction with Al slightly more than with Ni, while Hf shows a particularly strong affinity for Ni compared to Al. Sulfur's predicted weaker binding and ease of diffusion may also hint at its role in apparently weakening adhesion between metals and their corresponding oxide scales. Pt's and Hf's stronger interactions with the NiAl substrate may point to possible roles in stabilizing that same metal-oxide scale interface, as discussed next.

Effects of Segregating Elements on TGO-Bond Coat Interface Adhesion

We evaluated with DFT the structure and adhesion of the pure and doped α-Al2O3(0001)/NiAl(110) interface as a model for the TGO-bond coat alloy interface in TBCs [8]. We find that the clean interface has an ideal work of adhesion of 0.66 J/m², which is larger by 0.2 J/m² than the adhesion of α-Al2O3(0001) to Ni(111). The increased adhesion is due to formation of Al-O cross-interface bonds. *We find that S impurities reduce interfacial adhesion significantly (by ~80%!), due to a reduction in cross-interface bonds. The weakened adhesion and wide metal-oxide gap in the interface structure helps explain TEM*

6

measurements on TBCs that find S present near voids between the bond coat alloy and the oxide. The elongated, weakened bonds we find across the S-containing metal/oxide interface and apparent S-O repulsion may induce the oxide and metal to separate and form voids upon experiencing stresses introduced during thermal cycling of the TBC.

The presence of Pt, either substitutionally or interstitially, alters interface adhesion only slightly (actually weakening it by ~20%), thus ruling out a previously postulated direct role for Pt of improving TGO-bond coat adhesion. On the other hand, we find Hf dramatically increases TGO-bond coat alloy adhesion, by forming strong Hf-O bonds across the interface, as expected from Hf's open-shell character. Our earlier work found that early transition metals such as Ti and Zr improve adhesion for the Al_2O_3/Ni interface by up to a factor of two at high concentrations (0.5 ML). We now find that Hf increases the metal-oxide adhesion even more, by a factor of three, even at low concentrations (0.1 ML)! *Thus, one role for Hf as a dopant in TBCs is indeed a direct and dramatic increase in the intrinsic adhesive strength of the TGO-bond coat alloy interface. This explains why Hf is a preferred dopant over Ti or Zr, since the improvement in adhesion is most pronounced with Hf.*

Interaction of Dopants, Impurities, and Majority Elements with an α-Alumina Surface

We used DFT to investigate adsorption of Al, O, Hf, Y, Pt, and S atoms on the α-Al_2O_3(0001) surface [9, 10]. We find that Al, Hf, and Y preferentially adsorb on threefold hollow sites and transfer electrons to the three surface oxygen atoms. By contrast, the most stable adsorption site for Pt and S is on top of a surface oxygen atom, with little charge transfer. We find a binding energy ordering of S < Pt < O < Al << Y < Hf, which reflects the ease with which the early transition metals Hf and Y ionize and form a mixture of ionic, covalent, and donor-acceptor bonds, as well as reflecting the nearly closed-shell repulsions that weaken the adsorption of O, Pt and S. *The fact that Pt binds on the same site as S, but more strongly, suggests that one role for Pt may be to displace and/or block S from segregating to the interface. Likewise, Hf and Y bind to the same site as Al, but much more strongly, suggesting that another role for Hf and Y is to block Al sites, thereby inhibiting Al diffusion that is central to TGO thickening. Since O adsorbs on a different site, Hf and Y cannot inhibit O diffusion, which explains why these dopants slow down (by inhibiting Al diffusion) but don't shut off TGO growth. Lastly, we find that Pt does not inhibit adsorption of Al or O, which explains why Pt does not affect TGO growth kinetics.*

Effect of Pt on Defect Formation and Diffusion of Ni and Al in NiAl

Since we have been able to rule out a direct role for Pt in increasing adhesion of the TGO-bond coat interface, we have been exploring indirect roles, such as the one mentioned directly above where Pt may inhibit S's ability to segregate to the TGO-bond coat alloy interface. In addition, we are exploring whether the main role of Pt is to affect the high temperature evolution of the NiAl bond coat alloy. It is known that Pt hinders spinel formation even in high Ni content NiAl alloys. We wondered then whether Pt's

rols is to influence Ni and/or Al diffusion to the TGO interface in such a way as to preferentially promote formation of alumina rather than Ni spinel. We set out to use DFT to investigate these processes [11] and are writing up the first set of results that deal with Pt's effect on the formation of key defects central to postulated mechanisms of diffusion of Ni (and Al) through NiAl. These defects include Ni and Al vacancies and antisite atoms (Al atoms on the Ni sublattice and vice versa), and clusters of these defects that may facilitate diffusion [12]. Key findings so far are that Pt aggressively promotes formation of these defects, as evidenced by significant decreases in their formation energies. This suggests that Pt may facilitate Al diffusion, thereby keeping the Al concentration at the NiAl surface high enough to preferentially form alumina instead of the very brittle Ni spinel. In ongoing work, we are exploring Pt's effect on diffusion barriers to test this hypothesis.

Segregation of Dopants and Primary Elements to an Alumina Grain Boundary

We used DFT to characterize the structure and electronic properties of the $\Sigma 11(10\bar{1}\,\bar{1}) \| (10\bar{1}\,1)$ grain boundary [13], which has been characterized by TEM and has been observed to exhibit dopant segregation. We then mapped out favorable adsorption sites for Al, O, Y, and Hf atom at the grain boundary, evaluating segregation energetics and grain boundary strength as a function of segregating element. We found a new structure for the clean boundary that is lower in energy than previously proposed structures. In addition, we predict that Y and Hf segregation to the grain boundary should hinder the diffusion of Al by blocking its preferential adsorption sites. Yttrium also had the effect of doubling the grain boundary adhesion energy, consistent with the observation of reduced creep upon Y doping of alumina. Thus, once again we see that the role of the early transition metals is both the increase adhesion and to block diffusion of Al, thereby slowing the growth of the TGO in the TBC.

Catalyst Design Based on Metal-Ceramic Interface Characterization

Metal-ceramic interfaces are not only prevalent as protective coatings such as TBCs but are common in heterogeneous catalysis, where metal catalyst particles are bound to an oxide support. The support is typically alumina or silica, the same materials we examined for TBC applications. Ni/alumina catalysts are used for all sorts of chemical processing (methanation, hydrogenation of oils for making margarine, etc.). A classic problem is that catalysts often de-activate by sintering, where catalyst particles aggregate to form larger particles of low surface area. We had the idea that the sintering process might be inhibited if one could fasten the catalyst particles more tightly to the support. Hence adhesion characterization we did for TBCs earlier could be applied to this completely different technology. We filed a patent on the idea that one could dope the interface between a Ni-based metal catalyst particle and a silica or alumina support with early transition metals. The idea is that the early transition

8

metals promote stronger oxide-metal interactions via their open shell nature, which permits donor-acceptor bonding concomitant with metal-oxo and metal-metal polar covalent bonding. We had shown this to be true for alumina/nickel interfaces and postulated it to be true for other similar interfaces in the patent application [14].

Summary

During the last two years, we developed new theoretical methods for describing condensed matter [1,2] and uncovered some atomic level reasons for failure of thermal barrier coatings, including stress buildup due to phase transformations [3] and fatigue [4,5]. We explored adsorption and segregation of several dopants (Hf, Pt) and impurities (S) that are known players in TBCs [7,8]. We provided evidence that S indeed grossly weakens the key interface in TBCs, that Pt does not play a direct role in improving adhesion though it may block S from getting to the bond coat alloy-TGO interface, and that Y and Hf directly and greatly strengthen TBC adhesion as well as inhibiting TGO growth [8,9,10,13]. We also suggested that another role for Pt is to promote formation of key defects needed to facilitate the supply of Al to the alloy-TGO interface so that alumina rather than spinels form [11,12]. We continue to suggest how to improve TBCs [6] and thought of an industrial spin-off for catalysis [14].

Faculty:	Emily A. Carter, P.I.
Postdoctoral Fellows:	Dr. Karin Carling, Dr. Kyle Caspersen, Dr. Berit Hinnemann, Dr. Ivan Milas
Graduate Students:	Emily A. Jarvis, Vincent Cocula, Robin Hayes, De-en Jiang, Will Glover, Hakan Gunaydin, Tracy Mitchell, Kristen Marino
Collaborator:	Christopher Pickard, Accelrys, Inc.

AFOSR Publications and Patents (Jan. 1, 2005 – Dec. 31, 2006)

[1] K. J. Caspersen and E. A. Carter, "Finding Transition States for Crystalline Solid-Solid Phase Transformations," *Proc. Natl. Acad. Sci.*, **102**, 6738 (2005).

[2] V. Cocula, C. J. Pickard, and E. A. Carter, "Ultrasoft Spin-Dependent Pseudopotentials," *J. Chem. Phys.*, **123**, 214101 (2005).

[3] K. J. Caspersen and E. A. Carter, "Phase Transformation Path for Monoclinic to Tetragonal Zirconia: Origin of Temperature Hysteresis," manuscript in preparation (2007).

[4] R. L. Hayes and E.A. Carter, "Atomic Origin of Hysteresis During Cyclic Loading of Si Due to Bond Rearrangements at the Crack Surfaces," *J. Chem. Phys.*, **123**, 244704 (2005).

[5] E. A. A. Jarvis and E. A. Carter, "A Nanoscale Mechanism of Fatigue in Ionic Solids, "*Nano Letters*, **6**, 505 (2006).

[6] D. E. Jiang and E. A. Carter, "First Principles Study of the Interfacial Adhesion between SiO_2 and $MoSi_2$," *Phys. Rev. B*, **72**, 165410 (2005).

[7] K. M. Carling, W. Glover, H. Gunaydin, T. Mitchell and E. A. Carter, "Comparison of S, Pt, and Hf Adsorption on NiAl(110)," *Surf. Sci.*, **600**, 2079 (2006).

[8] K. M. Carling and E. A. Carter, "Effects of segregating elements on the adhesive strength and structure of the $\alpha Al2O3/\beta$-NiAl interface," *Acta Materialia*, in press (2006).

[9] B. Hinnemann and E. A. Carter, "Understanding aluminum oxide growth in thermal barrier coatings," *MHPCC Application Briefs*, 12 (2006).

[10] B. Hinnemann and E. A. Carter, "Adsorption of Al, O, Hf, Y, Pt, and S atoms on α-$Al_2O_3(0001)$, " *J. Phys. Chem.*, in press (2006).

[11] K. A. Marino and E. A. Carter, "The effects of platinum on thermal barrier coating performance," *MHPCC Application Briefs*, 10 (2006).

[12] K. A. Marino and E. A. Carter, "Effect of Pt on defect formation in NiAl: Implications for Pt's role in thermal barrier coatings," manuscript in preparation (2007).

[13] I. Milas, B. Hinnemann, and E. A. Carter, "Structure and Ion Segregation at an Alumina Grain Boundary: Implications for Growth and Creep," manuscript in preparation (2007).

[14] E. A. A. Jarvis and E. A. Carter, "Catalyst Doping to Strengthen Metal-Support Interactions," foreign and U.S. utility patent pending since 2003.

Ph.D. Dissertations

Emily A. Asche Jarvis, UCLA Ph.D 2002. Dissertation title: Atomic-level Culprits of Materials Failure: The Importance of Chemical Bonding at Heterogeneous Interfaces.

Vincent Cocula, UCLA Ph.D. 2004. Dissertation title: Spin-Dependent Pseudopotential Density Functional Theory.

Robin L. Hayes, UCLA Ph.D. 2004. Dissertation title: First-Principles-Based Multi-scale Modeling of Crystalline Materials Failure.

De-en Jiang, UCLA Ph.D. 2005. Dissertation title: Chemistry of iron surfaces and interfaces from first principles.

These dissertations are available upon request from UMI Proquest Digital Dissertations http://wwwlib.umi.com/dissertations/gateway; all results contained in the theses have been published in the open literature (see the list above).